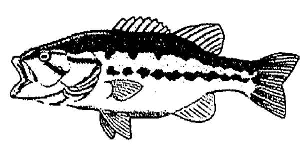
# 4. MERCURY





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## 4.1 SUMMARY

Mercury levels of certain species of fish in the Delta and San Francisco Bay are at sufficient concentrations to warrant fish advisories for human consumption. The mercury that has accumulated in the Delta and Bay, and continues to accumulate, may also be adversely affecting wildlife, both aquatic and terrestrial.

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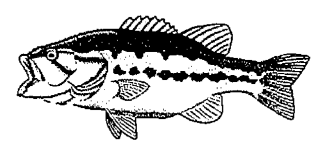
Information should be developed to document current mercury levels in water, sediment, and fish throughout the Bay, Delta, San Joaquin and Sacramento Rivers, Cache Creek, and other tributaries. This information can be used to assess mercury bioaccumulation in wildlife (especially sport fish), human exposure, and the ecologic and human impacts of mercury bioaccumulation. Documentation also could identify mercury sources and their remediation potential. Documentation would require a comprehensive monitoring program that should address the loadings and sources of total and methyl mercury, the amounts of sediment-carried mercury transported throughout the system, the forms and bioavailability of this mercury, and the concentrations of mercury in fish or other bioindicator species. This approach is needed to document the current status of mercury contamination in this system, as well as to provide a means to quantify the success of remediation efforts. In addition, a common database of existing mercury data, newly acquired mercury data, geographic spatial information, and accurate fate and mobility models are necessary to store and use the data as a basis for mercury management or other decisions affecting water quality.

The mercury issue is complex. For example, the total load of mercury is only one of several considerations for exposure assessment and cost-effective remediation. Studies are needed to address the current status of the processes (e.g., methylation) affecting mercury transformation and bioaccumulation in the Bay-Delta region. These studies need to address the source and forms of mercury currently transported in the Bay-Delta and whether or where they are bioavailable. These studies will provide a basis to prioritize remediation or clean-up of the sources of mercury that are currently leading to excessive bioaccumulation of mercury.



## 4.2 PROBLEM STATEMENT

Water quality problems associated with mercury occur on a global basis. The most serious problems, with respect to human health, occur when mercury accumulates in edible aquatic organisms. Mercury can be transported through the atmosphere from various emissions, such as power plants, or can enter aquatic systems in runoff from mining operations or in runoff from natural geological sources. A number of mercury sources are present in California, including mining, atmospheric, and geological.

Mercury has been found throughout the San Francisco Bay-Delta estuary at elevated concentrations in water, sediment, and organisms. Mercury is of concern from both an environmental and human health perspective. Effects on fish include death, reduced reproductive success, impaired growth and development, and behavior abnormalities. Mercury exposure in birds can cause reproductive effects, and in plants can cause death and sublethal effects. The direct and additive effects of mercury within the estuary on reproduction, development, and juvenile survival of aquatic and aquatic-feeding species are poorly understood.

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In general, mercury concentrates through aquatic food chains such that organisms in higher trophic levels accumulate higher mercury concentrations. Fish found at the top of the food web can exhibit mercury tissue concentrations over 1 million times the mercury concentration of the surrounding water. High mercury levels in sport fish have culminated in consumption advisories in which some consumers are advised to not eat these fish. Mercury (in the form of methyl mercury) poses a serious concern to human health as it accumulates in tissue, bioaccumulates within the food web, and is a potent neurotoxin in humans. Mercury can cause nervous system damage in developing fetuses, as well as in children and adults.

## 4.3 OBJECTIVE

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## 4.4 Problem Description

In 1971, DHS issued a health advisory recommending that pregnant women and children should not consume striped bass taken from the Bay-Delta estuary due to high mercury levels.

A 1994 fish tissue contamination study in the Bay revealed mercury concentrations in fish tissue in species other than striped bass that were of concern to human health. Based on evaluation of the results of this study (including levels of other contaminants of concern), in December 1994, the California Office of Environmental Health Hazard Assessment (OEHHA) issued advisories concerning consumption of fish caught from the Bay. Specifically, adults were advised to limit consumption of sport fish from the Bay to two times a month, and pregnant or nursing women and children 6 or under were advised to limit consumption to one time a month. Further, the advisory recommended that large shark and striped bass from the Bay should not be consumed at all.

The SWRCB's biennial water quality assessment lists 48,000 acres of Delta waterways as impaired because of fish consumption advisories for mercury. Water bodies (or segments) included on the CWA Section 303(d) impaired water bodies list due to mercury levels include: (1) in Delta waterways, Marsh Creek; (2) in the Sacramento River watershed, the lower American River, Cache Creek, the lower Feather River, Harley Gulch, Humbug Creek, the Sacramento River (from Red Bluff downstream to the Delta), Sacramento Slough, and Sulfur Creek; and (3) in the San Joaquin watershed, Panoche Creek, Salt Slough, and San Carlos Creek.

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In general, large-scale, systematic sampling of a variety of fish species has not been conducted in the Bay, the Delta, or in the Sacramento and San Joaquin River Basins. Proper protection of the public from mercury contamination requires comprehensive studies of sport fish species that are commonly caught and consumed in the Delta estuary. These studies should include monitoring the levels of mercury contamination in different species through several flow cycles at multiple sites in these waterways. The studies can be used to evaluate the public health risks of consuming different species at different sites throughout the region and to prioritize cleanup and remediation options. Comprehensive studies that can be used in a health evaluation also have not been conducted.

Elevated mercury levels also may have lasting effects on habitat and ecology in these waterways. In 1986, the CVRWQCB surveyed mercury contamination in fish and sediment in the Sacramento River watershed. The survey detected elevated mercury levels in sediment in the Yuba and Bear Rivers and in Cache, Putah, and Stony Creeks. Ongoing research by UC Davis has confirmed these streams as among those with the highest levels of bioavailable mercury, as measured with in-stream bioindicator organisms. Recent sampling by the USGS National Water Quality Assessment (NAWQA) Program has confirmed that elevated concentrations are still present in the sediments of the Yuba and Bear Rivers and in Cache Creek, as well as in the sediments of other streams and rivers in the Sacramento River Basin. Fish captured in certain tributaries contained mercury levels that exceeded the 1973 National Academy of Sciences guidelines to protect aquatic resources and their predators. The CVRWQCB also has determined that mercury has caused the impairment of aquatic habitat beneficial use of the Sacramento River between the Colusa Basin Drain and the Delta.

A 1997 report containing survey results of bioavailable mercury throughout the northwestern Sierra Nevada (the Feather River south to the Cosumnes River) found the most highly elevated mercury levels in the aquatic food webs of the South and Middle Forks of the Yuba River, the North Fork of the Cosumnes River, tributaries throughout the Bear River drainage, the mid-section of the Middle Fork of the Feather River, and Deer Creek. Similar surveys of mercury levels in sediment and their bioavailability to aquatic bioindicator organisms and wildlife should be extended throughout the Delta estuary. Such surveys will enable a full assessment of ecologic risks and facilitate prioritizing cleanup and remediation options.

## *4.4.1 Sources and Transport of Mercury*

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There is a wide assortment of anthropogenic sources of mercury. Mercury has been used globally in many industrial, agricultural, and domestic applications. For example, mercury is used in such products and processes as barometers, thermometers, mercury arc lamps, switches, fluorescent lamps, mirrors, catalysts for oxidizing organic compounds, gold and silver extraction from ores, rectifiers, and cathodes in electrolysis/electroanalysis; in the generation of chlorine and caustic paper processing, batteries, and dental amalgams; as laboratory reagents, lubricants, caulks, and coatings; in pharmaceuticals as a slimicide; and in dyes, wood preservatives, floor wax, furniture polish, fabric softeners, and chlorine bleach. Human-related sources of mercury include fossil fuel combustion, production of chlorine and caustic soda at chlor-alkali plants, waste incineration, cremation, industrial discharges flowing through sewage treatment plants, mines and mining activities, smelters, and mercury spills from naval vessels.

Mining-related activities are known to be a significant anthropogenic source of mercury within the estuary. The California Coast Ranges, on the west side of the Sacramento Valley, contain a large deposit of cinnabar; mines in this area supplied the majority of mined mercury in the United States. During the late 1800s and early 1900s, mercury was intensively mined from the Coast Ranges and subsequently transported across the Central Valley to the Sierra Nevada for use in placer gold mining operations. The majority of Coast Ranges mercury mines are now abandoned and remain unreclaimed. Some of the best known mercury mines are found in the Cache Creek and Lake Berryessa drainages in the Sacramento River watershed, in the San Joaquin River watershed, in the Marsh Creek watershed in the Delta (Mount Diablo Mine), in the South Bay watershed (New Almaden mining district), and in Panoche Creek (draining to the San Joaquin River from the New Idria mercury mining district). In addition to the active and abandoned mercury mines, many unmined mercury deposits (in the form of cinnabar or HgS) are found throughout the Coast Ranges. Natural springs occurring in the Coast Ranges also discharge mercury that has been mobilized by geothermal processes.

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The mercury used in gold mining in the Sierra Nevada was refined liquid quicksilver or elemental mercury. Virtually all of the mercury brought to the Sierra Nevada for gold mining was ultimately lost into Sierran watersheds; once back in the environment, this elemental mercury likely underwent various transformations into different forms. The CVRWQCB has estimated that approximately 7,600 tons of refined quicksilver were deposited in the Mother Lode region alone during the Gold Rush mining era. Mercury also was used in the northwestern and central Sierra Nevada for gold mining.

Much of the mercury used in gold mining could have been incorporated into the 12 billion cubic meters of sediments extracted by mining activities and released to the rivers of the Bay-Delta watershed. Studies by UC Davis and, more recently, by USGS show that the sediments mobilized by hydraulic mining ultimately were transported to the Bay-Delta, where they formed marshes and islands, or were deposited in shallow-water sediments. Some of these potentially mercury-contaminated areas now are being considered for habitat restoration through CALFED's Ecosystem Restoration Program. USGS studies show that mercury concentrations in Bay sediments containing hydraulic mining debris range from 0.3 to 1 $\mu$g/g. More importantly, these sediments contain mercury in its most reactive forms, including methyl mercury.

Recent studies suggest that the Coast Ranges may be a more significant contributor of mercury loadings to Central Valley rivers and the estuary than the Sierra Nevada. However, the relative contribution of these loads (dominated by cinnabar minerals) to mercury bioaccumulation, compared to the possibly more reactive mercury from the Sierra side of the valley (dominated by elemental mercury from placer gold mining) is unknown. Additional mercury may be introduced by industrial processes or runoff in urban centers.

Monitoring indicates that significant loading of metals to the estuary occurs during high-flow conditions. Sampling in the Sacramento River performed by the CVRWQCB in January 1995 during a peak storm period detected high mercury concentrations in the Yolo Bypass. (Water from the Sacramento Valley entered the estuary via both the Sacramento River and the Yolo Bypass during this storm period.) Further investigation determined that Cache Creek (which drains Clear Lake, an area with several mercury mines) appears to be a significant source of mercury discharging into the Yolo Bypass (and ultimately into the Delta) during heavy runoff events. Cache Creek was estimated to have exported approximately 1,000 kilograms (kg) of mercury to the estuary in 1995. Long-term, quantitative studies by UC Davis of just one tributary of Cache Creek (Davis Creek) have found annual loadings of 180-250 kg per year of newly deposited mercury. High mercury levels also were found in the Sacramento River upstream of the confluence with the Feather River. In addition, recent work by consultants to the Sacramento County Sanitation District, and confirmed by subsequent sampling by the USGS, has shown that an unknown source of mercury is present somewhere between Red Bluff and Colusa, and that the loading from this source following stormwater runoff is significant. The source and form of this mercury is unknown. Sampling by the USGS NAWQA program at the Yolo Bypass during the 1997 flood showed that the loading of mercury to estuary was approximately 32 kg per day at peak discharge. In contrast, mercury loadings to the Bay from the Sacramento River during the dry season are approximately 0.2 kg per day.

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Marsh Creek is another watershed in Contra Costa County with high mercury levels. Studies conducted in 1995 through 1997 determined that this relatively small watershed exported 10-20 grams of mercury per day, with greater amounts during storm events. These studies also found that approximately 95% of the mercury load of the entire extended watershed originated from the Mount Diablo Mine area, with 89% coming from a highly localized area of exposed mine tailings. Although considerably less than the Cache Creek loads, virtually all of the mercury load derived from the Mount Diablo mercury mine was found to originate in dissolved form, presumably highly available for microbial methylation, and ultimate movement and bioconcentration into the food web. Also notable was the finding that, although geologically naturally enriched in mercury, the natural watershed did not contribute significantly to the mobilized, annual storm-associated loadings of mercury. Mine wastes were found to greatly dominate the overall loading.

Mercury transported from these watersheds is deposited in the Bay-Delta. Depositional areas ranging from the Yolo Bypass to Suisun Marsh have the potential to be important sources of mercury methylation. These areas may be a more significant source of the methyl mercury found in fish than the new mercury coming from the mines. Mercury in sediment may be resuspended through bioturbation, wave action, dredging activities and disposal, and flooding of lands. The chemical form of mercury in the sediment and environmental conditions at the time of release will affect the bioavailability of the reintroduced mercury.

Bulk mercury contamination is extensive on both sides of the Central Valley, primarily widely scattered hydraulic mining debris on the east side, and active and abandoned mines and associated debris piles on the west side. Cumulatively, these activities have resulted in the ongoing deposition of significant amounts of mercury in sediments of the Bay-Delta system.

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Determining the relative contributions of the various sources (mercury mines, hydraulic mining debris, and recycling from depositional areas) to the primary problem (methyl mercury in fish) is essential before cost-effective solutions to the region's mercury problems can be developed.

## *4.4.2 Transformation and Bioavailability of Mercury*

Mercury occurs naturally within the environment in a variety of forms, including elemental mercury (Hg[0] or quicksilver); dissolved in rainwater ($Hg^{+2}$); as the ore, cinnabar (HgS); and as methyl mercury ($HgCH_3$), an organo-metal. Mercury can undergo biological and chemical reactions that cause it to change form and alter its solubility, toxicity, and bioavailability. Toxicity depends primarily on the particular form of mercury. Methyl mercury is the most toxic form of mercury to animals and humans, and is created in the environment by microbes under appropriate conditions.

Methylation of mercury is a key step, enabling the entrance of mercury into food chains. Nearly 100% of the mercury that bioaccumulates in fish tissue is in the form of methyl mercury. The biotransformation of inorganic mercury into methylated organic mercury in water bodies occurs in both the sediment and the water column. Many factors affect the formation of methylated mercury, including pH, temperature, oxygen/redox level, salinity, toxicity, rate of sediment deposition, rate of pore water diffusion (or the rate at which methyl mercury diffuses out of the sediment and into the water), rate of mercury deposition, species of mercury deposited, and the rate of methyl mercury removal by bioaccumulation and other biological processes including de-methylation.

As stated above, the predominant form of mercury varies within the Delta estuary. Elemental mercury from gold mining activities is prevalent in drainage from the Sierra side of the valley, while cinnabar predominates in loadings from the Coast Ranges side of the valley. Determining the relative transformation and bioavailability of these different forms throughout the watershed, in addition to their sources and loadings, will be important for prioritizing remediation options. For example, recent water quality data indicate that a significant amount of mercury from the gold mining era still exists in the sediment of the Upper Yuba River watershed, which is then transported downstream into Englebright Reservoir, where it is largely contained. Bioavailability studies by UC Davis reveal that the reservoir intercepts both inorganic, sediment-based mercury as well as bioavailable methyl mercury. While elevated mercury levels have been found upstream and in the reservoir, aquatic organisms taken from below the dam consistently demonstrate lower levels of mercury than those organisms in the reservoir or upstream. This finding suggests that the reservoir serves as an interceptor of bioavailable mercury, preventing it from being transported downstream to the estuary. This finding also may indicate that much of the mercury in the Sierra Nevada remaining from gold mining activities, at least that originating upstream in dammed tributaries, may be trapped in foothill reservoirs and prevented from reaching the estuary. However, mercury bioaccumulation in these reservoirs may still pose localized health risks that should be evaluated.

Studies of mercury transformation, methylation, and bioavailability must be extended throughout the watershed and include the Bay-Delta. Research is needed to determine the methylation capability of Bay-Delta sediments, particularly those sediments that originated from hydraulic mining activities. Flooding or disturbing such sediments could inadvertently increase the amount of methyl mercury in the Bay ecosystem (i.e., uninformed restoration activities could augment the mercury contamination of Bay fish). Numerous instances of accelerated methylation have occurred when sediments were flooded for reservoirs elsewhere, even in the absence of the type of mercury contamination found in hydraulic mining debris.

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## 4.5 APPROACH TO SOLUTION

### 4.5.1 *Priority Actions*

Since it is well documented that mercury is an important contaminant in the Bay-Delta estuary that can affect humans and wildlife, it is appropriate that a coordinated and well-planned effort be implemented to determine the extent of the problem and cost-effective solutions for remediation. This effort requires a broad step-wise approach. Initially, a thorough risk appraisal should be conducted for the Delta estuary, including the major rivers and their tributaries, to determine the extent of the problem and risks to humans and wildlife. A related assessment should be conducted to determine the major sources of mercury and to follow its transport and transformation to biologically available forms. The information gathered in these steps would be used to formulate a variety of remediation and risk management strategies and to increase public awareness and education. The next step would be to implement remediation strategies expected to result in the greatest short-term effect and follow these with longer term strategies. A final component of this approach would be to demonstrate the effect of the remediation strategies by showing a reduction in mercury loading, transport, transformation, bioavailability, and bioaccumulation. **No remedial activities on abandoned mine sites should be conducted without federal environmental "Good Samaritan" protection. Without this protection, acting CALFED agencies may become responsible parties for the abandoned sites.**

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It is envisioned that this approach would involve three stages, as outlined below.

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### *Stage I - Data Collection, Evaluation, Planning, and Remediation Demonstration (probably a 5-year approach)*

**Fish tissue monitoring for impacts on human health and wildlife**

Evaluate existing fish tissue data for mercury, with a focus on the risks to humans and wildlife.

Identify data gaps and needs (e.g., multi-site, multi-species, and multi-year data) for fish tissue and wildlife monitoring.

Plan and undertake monitoring to fill data gaps.

Investigate fish consumption patterns (e.g., species) in the watershed to better characterize human exposure due to fish consumption.

Using new and existing data, evaluate human risks throughout the Delta estuary due to consumption of fish contaminated with mercury. Identify local versus widespread risks. Consider whether risks require local or widespread remediation efforts. Include evaluation of acceptable levels of mercury in sediment and water.

Using new and existing data, evaluate wildlife risks throughout the Delta estuary due to mercury contamination. Identify local versus widespread risks. Consider whether risks require local or widespread remediation efforts. Include evaluation of acceptable levels of mercury in sediment and water.